Adsorption and Nanoscale Magnetic Separation of Heavy Metals from Water

James D. Navratil
Clemson University
Environmental Engineering and Science
342 Computer Court
Anderson SC 29625-6510
Phone: 864-656-1004
Fax: 864-656-0672
Email: nav@clemson.edu

One of the primary needs of mankind over the next millennium is improved and less expensive water treatment methods. Recent efforts by the United States Environmental Protection Agency (USEPA) have focused on reducing the concentration levels of arsenic in drinking and wastewater treatment plants. Thus we are developing a new and inexpensive magnetic filtration/adsorption technology for purifying water supplies that is not only in line with mankind's future needs, but may also alleviate the problems with arsenic identified by the USEPA. This nanolevel high gradient magnetic separation (HGMS) process is based on the use of a supported surface complex adsorbent such as natural magnetite ($FeO^.Fe_2O_3$) in a fixed bed mode. Due to its ferromagnetic property, magnetite can be used not only as an adsorbent for removing toxic metals from solution, but also as a magnetically energizable element for attracting and retaining paramagnetic nanoparticles, thus removing them from solution. In such a system, the inexpensive magnetite serves as a metal ion adsorbent, high gradient magnetic filter, or both, depending on the characteristics of the aqueous stream to be purified.

INTRODUCTON

Many processes have utilized iron oxides for the treatment of liquid wastes containing radioactive and hazardous metals. These processes have included adsorption, precipitation and other chemical and physical techniques [1-4]. For example, a radioactive wastewater precipitation process includes addition of a ferric hydroxide floc to scavenge radioactive contaminants, such as americium, plutonium and uranium [5]. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite [6]. Ferrite is a generic term for a class of magnetic iron oxide compounds [7]. Ferrites posses the property of spontaneous magnetization and are crystalline materials soluble only in strong acid. Iron atoms in iron ferrite ($FeO^.Fe_2O_3$) can be replaced by many other metal ions without seriously altering its spinel structure [8].

Various ferrites and natural magnetite were used in batch modes for actinide and heavy metal removal from wastewater [8-12]. Supported magnetite was also used in a column mode, and in the presence of an external magnetic field, enhanced capacity was found for removal of plutonium and americium from wastewater [13-15]. These observations were explained by a nanolevel high gradient magnetic separation (HGMS) effect, as americium, plutonium and other hydrolytic metals are known to form colloidal particles at elevated pHs [15]. Recent modeling work supports this assumption and shows that the smaller the magnetite particle the larger the induced magnetic field around the particle from the external field [16]. Other recent studies have demonstrated the magnetic enhanced removal of cobalt and iron from simulated groundwater [17,18].

The magnetic field-enhanced filtration/sorption process differs significantly from magnetic separation processes used in the processing of minerals, and more recently, for water treatment and environmental applications. Conventional processes use, for example, a fine stainless steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this reason, in order for such processes to remove metal ions and nanoparticles from solution, precipitating or flocculating agents must first be added to effect formation of large particles. In contrast, the magnetic filtration/sorption process is unique because a

highly porous adsorbent material not only acts as a magnetic matrix; it also contributes an adsorptive component to the system. This adsorptive component allows for the removal of complex metal species and ions from solution, while the relatively low field magnetic matrix allows for the removal of nanoparticles through a HGMS effect.

This paper will review previous work on the use of iron oxides for wastewater treatment and work leading to the development of the magnetic filtration/sorption process. A conceptual magnetic device and its operation options will also be presented along with a discussion of its potential for simple and inexpensive water and wastewater treatment.

FERRITE WASTEWATER TREATMENT

Metals are removed in most conventional wastewater treatment processes in the form of metal hydroxides since they have low solubilities. As noted above, ferric hydroxide is often added to scavenge a wide variety of heavy metal contaminants [19]. However, the metal hydroxide solids can form gelatinous precipitates, which are difficult to filter. Consequently, filter aids must sometimes be added to facilitate the filtration process.

The use of iron ferrite and magnetite in wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal [8]. Ferrite solids are crystalline materials, unlike hydroscopic metal hydroxide sludges, and can be more readily filtered; and their ferromagnetic character permits use of magnetic separation of the solids from solution. A wide variety of metal ion impurities can be effectively removed in one treatment step, and their removal is not seriously affected by high salt concentrations [8, 12]. The ferrite method does not require expensive chemicals, and since iron is usually a constituent of waste solutions, its oxidation states can be adjusted by chemical or electrolytic means to form ferrite. In situ and preformed ferrite methods have been used in wastewater treatment applications [8].

Most commonly with the in situ method, ferrous ion is added to the waste solution (usually heated to between 60° and 90°C) followed by the addition of base and subsequent oxidation (usually by aeration), and ferrite is formed within the waste solution itself. In this technique,

metal ions undergo ferrite formation and can be incorporated into the lattice of ferrite crystals. In the preformed case, ferrite is prepared separately using the in situ procedures described above and added in solid or slurry form to the waste solution. Magnetite, a naturally occurring ore and very prevalent in most parts of the world, can also be used in place of preformed ferrite. However, natural magnetite needs activation to have the same capacity as preformed ferrite [13].

The ferrite functions as an adsorption medium to remove contaminating species from solution. In situ ferrite can also function in this manner in addition to its chemical incorporation capabilities. The adsorption mechanism of ferrite occurs through metal hydroxide species. In alkaline solution, most metal ions form insoluble species, which may be complexed with additional hydroxide ions, depending upon the chemistry of the metal and the pH of the solution. Hydroxide ions are strongly adsorbed onto the surface of ferrite particles, so that metal ions can bond to the ferrite surface through the hydroxide ions to which they are bound. Alkali, alkaline and other metals, which do not form insoluble hydroxides, and metals which form soluble hydroxide complexes at high pH, such as aluminum and zinc, also are not removed by ferrite.

SUPPORTED MAGNETITE PROCESS
Magnetite from natural and waste sources is usually only available as a fine powder. To achieve low back-pressure and good water flow in a column of the magnetite, it must be supported with another material. The first tests of supported magnetite involved using a column containing a nonporous polyamine-epichlorohydrin resin bead coated with activated magnetite surrounded by an electromagnet of 0.3 Tesla [13]. In this work, the capacity of the magnetite coated resin for both plutonium and americium removal from water increased by a factor of five compared to using unsupported magnetite particles in the absence of a magnetic field.

The above observations were explained by a nanolevel HGMS effect, as americium, plutonium (and other hydrolytic metals) are known to form colloidal particles under alkaline conditions [15]. The pores of the magnetite-coated resin are large enough to permit the free displacement of the colloidal particles. When the field of the electromagnet is turned on, the magnetite particles are magnetically induced; creating a field

that contributes to the net field sensed by the colloidal particles. When the magnetic force is sufficiently greater than the force associated with Brownian (thermal) motion, the magnetic force created by the field can be attractive and sufficiently large to allow the magnetite to sorb the colloidal particles, provided they have sufficient magnetic susceptability. Recent modeling work has shown that the smaller the magnetite particle the larger the induced magnetic field around the particle from the external field [16]. When the electromagnet is turned off, the nanoparticles are released and dispersed in solution by thermal motion (metal hydroxide complexes would still be adsorbed, however, and would have to be removed by an eluent solution).

Recent studies have demonstrated the magnetic enhanced removal of cobalt and iron from simulated groundwater [17]. These preliminary results also indicate that natural components of groundwater, such as calcium and magnesium, do not interfere and are not removed with the process. Several suitable support media including glass beads were tested for mixing with natural magnetite that achieves satisfactory flow characteristics while retaining the magnetic field-enhanced sorption properties of magnetite [18].

CONCEPTUAL DEVICES AND PROCESS OPERATION
One inexpensive device for containing supported magnetite is simply some type of static-bed column with screens at the entrance and exit for holding the support in place while permitting the flow of smaller magnetite particles in and out of the column. The first step in operating the column would be to pass a slurry of activated magnetite down the column containing a support material such as glass beads [18]. Once the column is loaded with magnetite, the magnets would be placed around it to hold the magnetite in place. Then water to be treated would be passed upflow through the column until contaminant breakthrough is reached. Then the magnetic field would be removed and an additional amount of fresh magnetite slurry added to the top of the column to displace a portion of loaded magnetie and the captured contaminate particles. Then the magnets would be replaced around the column and more water passed upflow. The spent magnetite could be regenerated or discared depending on the contaminants and operational situation. Discarding the material would be useful for contaminants that sorb strongly onto the adsorbent material (thus perhaps serving as a favorable waste form for final disposal.

In some cases it may be advantageous to have the magnetite bonded to the support and to use a normal fixed-bed column operation with regenerating solution. There are several methods available to adhere or bond the magnetite particles onto supports. For example, crushed glass and glass wool may be mixed with the support in the presence of a solution of a alkali or alkaline hydroxide (this process would also activate the magnetite); heating may also assist the process, as well as raising the temperature to near the melting point of the glass without the solution present. Grinding the glass wool (or waste fiberglass insulation) with the magnetite may also bond the materials, as would the use of silica gel, resins and other bonding adhesives.

Besides supporting magnetite on inexpensive supports such as sand, crushed glass, glass beads or wool, etc, some supports could have adsorption characteristics that magnetite does not possess. Examples of these types of supports include selective inorganic ion exchangers, such as zeolites to sorb cesium, strontium etc., and activated carbon particles and fibers to adsorb dissolved organic compounds from solution. A layer of finely divided iron metal at the column inlet could be utilized to reduce certain metal ions, such as chromium, to a more insoluble form, and to form ferrites on the iron surface from the adsorption of ferric ions. Ferrites could also be prepared insitu as described above to enhance removal of certain contaminants. If metals would require removal in their higher oxidation states, air sparging or addition of oxidizing agents could be used to pre-treat the water.

Besides ferrite treatment, wastewater could also be pretreated with standard flocculation/precipitation and filtration steps to remove gross amounts of metal ions from solution. The magnetic filtration/sorption device would then be used as a polishing step for the water to remove colloids, small particles and complex ions not removed in the precipitation/filtration steps.

The column configuration and material of construction may improve the cost, operation and efficiency of the process. For example, in third world countries, columns could be constructed of plastic water bottles of various types. If the magnet is rectangular in shape, then thin rectangular columns may be more effective than cylindrical columns, and several devices run in parrallel may be advantagous with a row of columns sandwiched with fixed magnets.

CONCLUSIONS

Iron oxides in various forms have been used in water and wastewater treatment technology. The use of ferrites and magnetite has some advantages for batch treatment of a broad range of aqueous wastes. Activated magnetite, supported and used in a column mode in the presence of an external magnetic field, shows enhanced capacity in removal of a wide variety of contaminants from wastewaters. The magnetic field-enhanced filtration/sorption process shows promise as an improved, simple and inexpensive method for treating water and wastewater.

ACKNOWLEDGEMENTS

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